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Selective oxidation of dual phase steel after annealing at different dew points

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ABSTRACT

Hot galvanized steels have been extensively used in the automotive industry. Selective oxidation on the steel surface affects the wettability of zinc on steel and the grain orientation of inhibition layer (Fe–Al–Zn alloy) and reduces the iron diffusion to the zinc layer. The aim of this work is to identify and quantify selective oxidation on the surface of a dual phase steel, and an experimental steel with a lower content of manganese, annealed at different dew points. The techniques employed were atomic force microscopy, X-ray photoelectron spectroscopy, and glow discharge optical emission spectroscopy. External selective oxidation was observed for phosphorus on steel surface annealed at 0 °C dp, and for manganese, silicon, and aluminum at a lower dew point. The concentration of manganese was higher on the dual phase steel surface than on the surface of the experimental steel. The concentration of molybdenum on the surface of both steels increased as the depth increased.

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1. Introduction

Hot galvanized steels have been extensively used in the automotive industry due to their excellent corrosion resistance, good weld ability and good formability. The quality of galvanized layers is related to the characteristics of substrate such as chemical composition, microstructure, and surface condition as well as the characteristics of zinc bath and the operational conditions. The presence of scratches, iron powder, dirt, oil flecks on the steel surface, high roughness, and oxide formation affect the reactions at the coating/substrate interface inducing several defects in the final product. Oxidation on the surface can be produced due to the pickling process, high time of storage between cold-rolling and galvanizing, and processing in the galvanizing line.

Despite the protective atmosphere of the annealing furnace, selective oxidation of aluminum, silicon, manganese, boron, phosphorus, and iron, and precipitation of second phase particles such as boron and titanium nitride can occur during the thermal treatment of rolled plates. Especially in steels of high mechanical resistance which contain high contents of alloy elements, the susceptibility of selective oxidation increases. Selective oxidation affects the wettability of zinc on steel and the grain orientation of inhibition layer (Fe–Al–Zn alloy) and reduces the iron diffusion to the zinc layer. Parezanovic and Spiegel [1] reported that the oxides grow in the form of islands rather than in a continuous layer, and are not completely removed in the reduction-annealing step before galvanizing. An important aspect of these particles is that they can grow selectively depending on the grain orientation of the steel.

Bordignon and Crahay [2] report the reduction of wettability of zinc on steel, with the increase in the contact angle, due to the increase of oxygen content in a gaseous protective atmosphere in the furnace.

The most important parameter to control oxidation is the dew point of the reduction-annealing atmosphere. Changing the dew point allows the amount of water in the annealing atmosphere to be controlled. As well as the annealing conditions, Hertveldt et al. [3] reported that the steel composition plays an important role in the oxidation.

Dual phase steel is a high-strength steel that has a soft ferrite matrix containing islands of martensite as the secondary phase (martensite increases the tensile strength). The desire to produce high strength steels with formability greater than micro alloyed steel led to the development of dual phase steel in the 1970s. Chakraborti and Mitra [4] developed duplex ferrite–martensite

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Table 1
Chemical composition of steels (wt%).

Steel	C	Mn	Si	P	S	Al	Mo	Nb	N	O
Dual phase	0.12	1.83	0.013	0.020	0.0041	0.053	0.17	0.021	0.0046	0.0017
Experimental	0.13	0.79	0.011	0.022	0.0029	0.045	0.17	0.021	0.0055	0.0016

(DFM) steels containing 38–80% martensite of varying morphologies by batch intercritical annealing of a commercial variety vanadium bearing 0.2% C–Mn steel at different temperatures. Tensile test results revealed best strength–ductility combination for finely distributed lamellar ferrite–martensite phase aggregate containing 60% martensite developed from a prior martensitic structure.

The aim of this work is to identify and to quantify selective oxidation on the surface of dual phase steel, and a modified steel with a lower content of manganese, which were annealed at three dew points, using atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and glow discharge optical emission spectroscopy (GDOES).

2. Material and methods

Samples of two steels with 5 cm in diameter were taken from a cold rolled steel sheet. The chemical composition of the steels is shown in Table 1. Steel 1 is a dual phase steel, and steel 2 is modified steel with a lower content of manganese. The mechanical resistance limit of dual phase steel is 800 MPa.

Samples were annealed at 800 °C in a 5% (wt) H_2–95% (wt) N_2 atmosphere with dew points of −60, −30 and 0 °C. The annealing cycle consisted of several stages: heating, soaking time, slow cooling, fast cooling, over aging, and secondary cooling. The steel samples were put in furnace and were heated up to the soaking temperature. The heating rate was 10 °C s^{-1} and the final temperature was 800 °C. Soaking time was 80 s. In the slow cooling stage, the atmosphere was cooled with a recirculated hydrogen-nitrogen stream. The steel sheets were cooled up to 675 °C at a rate of −6 °C s^{-1}. In this stage, the transformation of austenitic grains into ferritic grains occurred.

In the fast cooling stage, the steel samples reached a temperature of 410 °C, at a rate of −8.1 °C s^{-1}. The objective of fast cooling is to adequate the carbon content in a solid solution, ensuring the transformation of the intercritical austenite to martensite.

Steel aging caused the loss of mechanical properties. The aim of over aging is to promote carbon precipitation, maintaining the steel at 410 °C for 180 s.

In the secondary cooling, the steel sheets were cooled to a temperature of 160 °C at a rate of −9.2 °C s^{-1} using streams of recirculated hydrogen-nitrogen gas mixture.

At the end of the annealing process, the steel samples were vacuum packed.

Characterization of the steel surface was performed by using atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and glow discharge optical emission spectroscopy (GDOES). X-Ray photoelectron spectroscopy (XPS) allows the determination of atomic composition of the sample in a non-destructive manner, as well as other chemical information, such as binding constants, and oxidation states of the different elements. Glow discharge optical emission spectrometry (GDOES), which is an optical emission spectrometry by using glow discharge plasma, gives the quantitative depth distribution of elements in a thin surface film formed on a metallic material.

An AFM analysis was performed using the Dimension 3000 microscopy, Digital Instruments, operating in contact mode using silicon nitride commercial probes.

The microstructure of steels was evaluated by using optical microscopy and the phases of steels were quantified by using the Axio Vision Digital Image Processing Software, a Carl Zeiss imaging system.

A GDOES analysis was performed using a SHIMADZU spectrometer, GDLS–9950 model. An XPS analysis was performed using a MICROLAB spectrophotometer, 310 F model, VG Scientific, and the X ray source was equipped with a magnesium target.

3. Results and discussion

3.1. Optical microscopy analysis

The microstructure of dual phase steel is shown in Fig. 1. The quantitative analysis of the steels showed that the dual phase steel has 66% of ferrite and 34% of second phases, martensite, austenite and carbides. The decrease of the manganese content of the dual phase steel promoted the increase of the ferrite content from 66% to 85% in the modified steel.

3.2. Atomic force microscopy analysis

Dual phase steel (steel 1) and the experimental steel (steel 2) showed oxide agglomeration on their surfaces after annealing at the dew points studied. The dual phase steel surface annealed at 0 °C dp is showed in Fig. 2. Drillet et al. [5] reported that in steels with a higher content of elements such as manganese and silicon, oxygen penetration and internal oxidation were reduced; and oxidation occurred on the surfaces of both steels.

3.3. Glow discharge optical emission spectroscopy results

External oxidation of phosphorus was observed at the highest dew point, when the content of oxygen was the highest according to Parezanovic and Spiegel [1]. As the oxygen concentration decreased, at lower dew points, oxidation of phosphorus did not

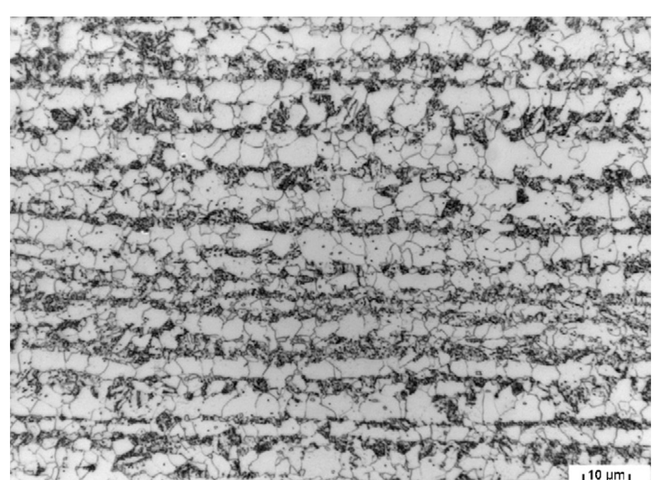

Fig. 1. Micrography of dual phase steel.

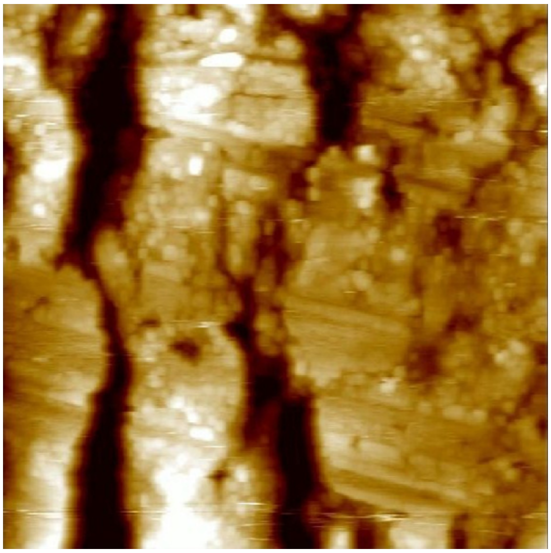

Fig. 2. AFM image of the dual phase steel surface annealed at 0 °C dp.

occur. Phosphorus was not found on the surface of both steels annealed at −30 °C dp. Hertveldt et al. [6] reported that at this temperature, phosphorus was in the grain boundary and did not produce oxides.

Manganese content on the steel surfaces was higher at lower dew points. Fig. 3 shows the content of manganese on the surface of the experimental steel annealed at −60, −30 and 0 °C dp. At lower oxygen contents, external oxidation of manganese, silicon, and aluminum occurred at lower dew points. Ramadeva et al. [7] and Hertveldt et al. [6] reported a higher external oxidation of manganese at lower dew points in the annealing processing. Parezanovic and Spigel [1] studied selective oxidation of an interstitial free and dual phase steel, and observed the same behavior for aluminum. The superficial concentration of manganese was higher on the dual phase steel surface than on the surface of the experimental steel, which showed a lower content of manganese (0.79% wt) than the dual phase steel (1.83% wt).

The content of molybdenum was highest on the surface of the experimental steel annealed at −60 °C dp and in the sub-superficial region of the experimental steel annealed at the dew point of 0 °C, as shown in Fig. 4. Molybdenum concentration increased as the depth increased from the surface of both steels (Fig. 4). The oxides of metals or alloys with good resistance to high temperature corrosion generally have a high melting temperature. They therefore remain in the solid state under typical working conditions. However, there are several exceptions to this rule. Landolt [8] reported that the melting point of MoO_3 is 795 °C, and temperatures of annealing reached 800 °C. Once liquid, these molybdenum oxides can dissolve other oxides that normally resist at these temperatures, and thus they accelerate the corrosion rate. The melting of molybdenum oxide can cause depletion of molybdenum on the surface.

Aluminum content on the dual phase steel surface was highest at the dew point of −60 °C (Fig. 5). Parezanovic and Spigel [1] observed that the aluminum concentration on the steel surfaces increased with the decrease of the dew point of the annealing. Eynde et al. [9] investigated the influence of water vapor concentration in the protective atmosphere of annealing on selective oxidation of dual phase steel without boron. Eynde et al. [9] reported that as the dew point decreased, the steel surface was enriched in aluminum and silicon. At −60 °C dp, the oxygen content is lower than at 0 °C dp, facilitating the external oxidation of reactive elements such as aluminum. As the oxygen content increases the change of external oxidation to internal oxidation occurs. Aluminum was not identified on the surfaces of the experimental steel, which shows a lower content of aluminum (0.045% wt) than the dual phase steel (0.053% wt).

3.4. X-ray photoelectron spectroscopy (XPS) results

The steel samples studied showed Mn 3s peak relative to the MnO_2 at the dew points of −60 °C, −30 °C (Fig. 6), and 0 °C (Fig. 7). For both steels, the Mn 3s peak presented the lowest intensity at the dew point of 0 °C. These results are in accordance with the GDOES results and literature data. The Mn 3s peak showed the highest

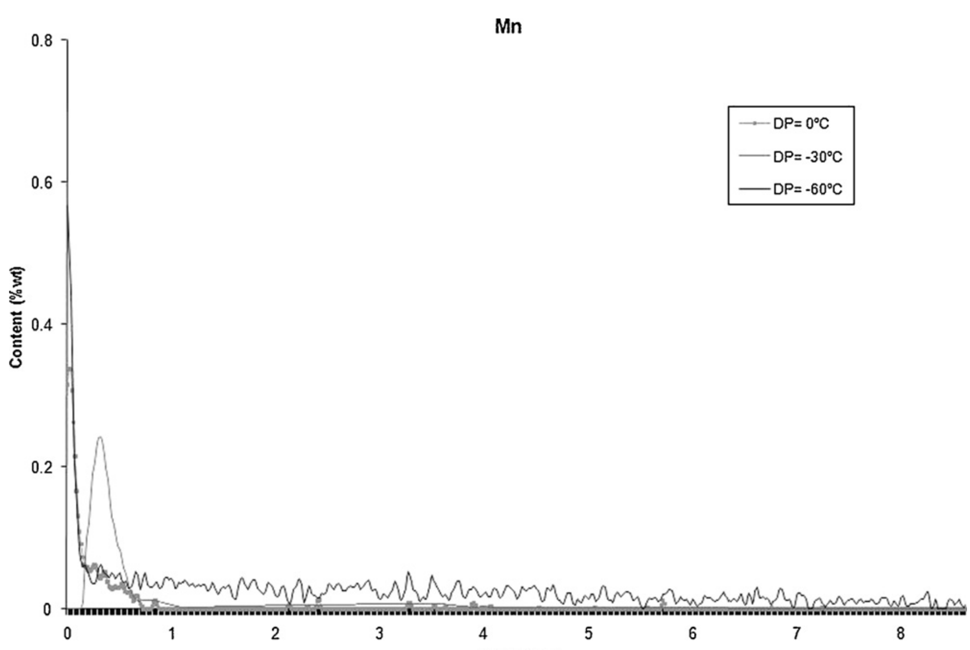

Fig. 3. GDOES spectra of manganese on the surface of the dual phase steel annealed at −60, −30 and 0 °C dp.

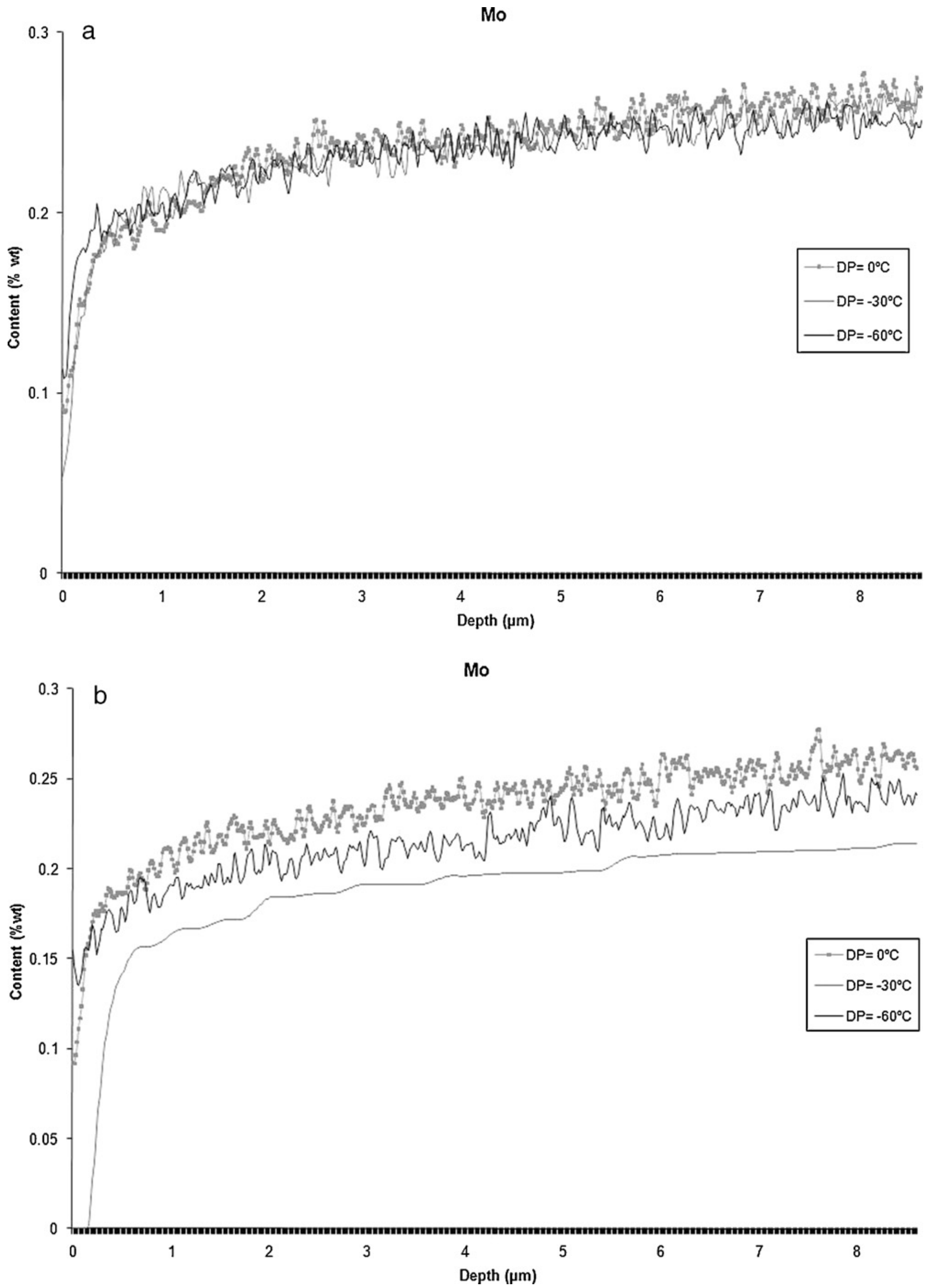

Fig. 4. GDOES spectra of molybdenum on the surface of the dual phase steel (a) and the modified dual phase steel (b) annealed at −60, −30 and 0 °C dp.

intensity for the dual phase steel (steel 1), which showed higher manganese content than the experimental steel (steel 2) as shown in Figs. 6 and 7.

A Mn 2p3 peak was identified at 641.5 eV, which corresponds to MnO or Mn_3O_4, and showed the highest intensity at the dew point of −30 °C. The Mn 2p3 peak showed the lowest intensity at −60 °C dp for the dual phase steel. Hertveldt et al. [3] and Parezanovic and Spiegel [10] reported that the manganese oxidation is higher at −30 °C.

Phosphorus was not identified at −30 °C dp. According to Hertveldt et al. [6], at this condition, phosphorus was localized in grain boundaries and did not produce oxides. At the dew points of −60 °C and 0 °C, the P 2p peak was observed and corresponded to the manganese-phosphorus oxides, showing the highest intensity after annealing at 0 °C dp. This observation is according to the GDOES analysis and confirms the data reported by Parezanovic and Spiegel [1]. Fig. 8 shows P2p spectra of steels annealed at 0 °C dp. Hertveldt et al. [3] also reported the occurrence of manganese-phosphorus oxides at higher dew points (10 °C). Erhart and Grabke [11] investigated the equilibrium grain-boundary segregation of phosphorus in Fe–P, Fe–C–P, Fe–Cr–P, and Fe–Cr–C–P alloys after annealing at temperatures in the range 400–800 °C. The authors confirmed the concentration of phosphorus at the grain-boundaries by using Auger electron spectroscopy on the intergranular fracture surfaces. In Fe–C–P alloys grain-boundary segregation is affected by site competition. Increasing carbon content of the samples causes

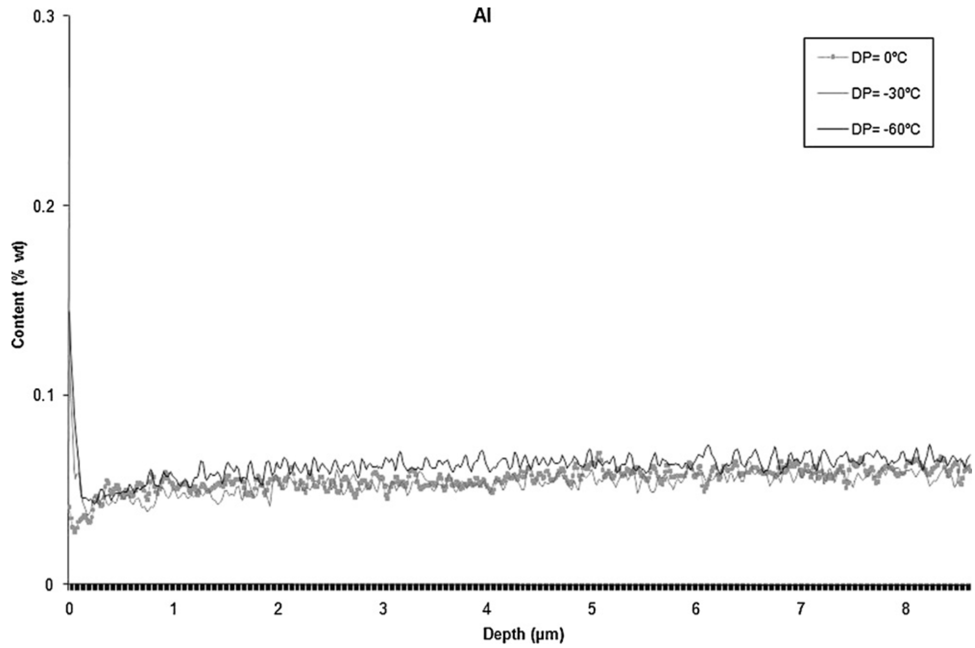

Fig. 5. GDOES spectra of aluminum on the surface of the dual phase steel annealed at −60, −30 and 0 °C dp.

an increase of the carbon concentration and a decrease of the phosphorus concentration at the grain boundaries. The grain boundaries segregation of phosphorus inhibits the oxidation of phosphorus.

Aluminum oxide was detected on the surface of both steels. The Al 2p peak, which is relative to Al_2O_3, had the highest intensity at the dew point of −60 °C. This peak was not identified at 0 °C dp for both steels. Parezanovic and Spiegel [1] reported the decrease of the aluminum signal with the increase of the dew point due to the change from external oxidation to internal oxidation. Eynde et al. [9] also reported the reduction of the aluminum content on the steel surface as the dew point was increased. Fig. 9 shows XPS spectra (Al 2p peak) of steels annealed at −60 °C dp.

The Si 2p3 peak at 102.5 eV relative to the manganese-silicon oxide was identified on the surface of both steels at the dew points of −60, −30, and 0 °C. Parezanovic and Spiegel [10] also reported the selective oxidation of silicon for steels with and without boron,

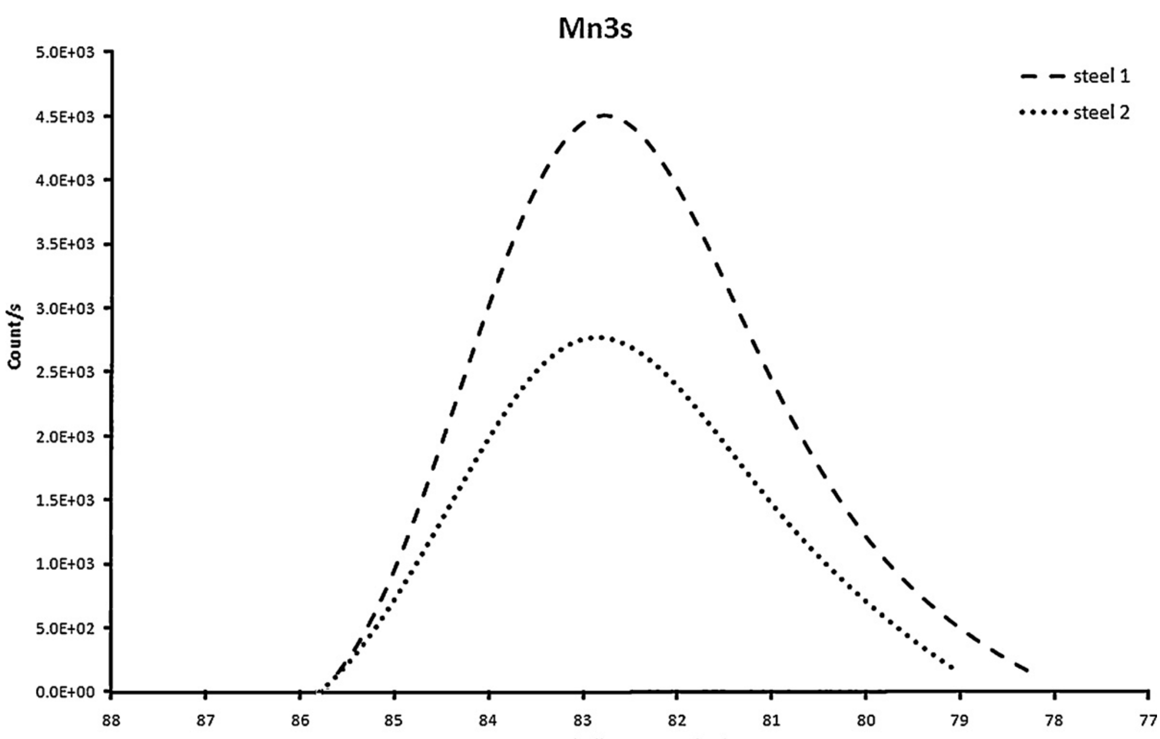

Fig. 6. XPS spectra of Mn3 s for the steels annealed at −30 °C dp.

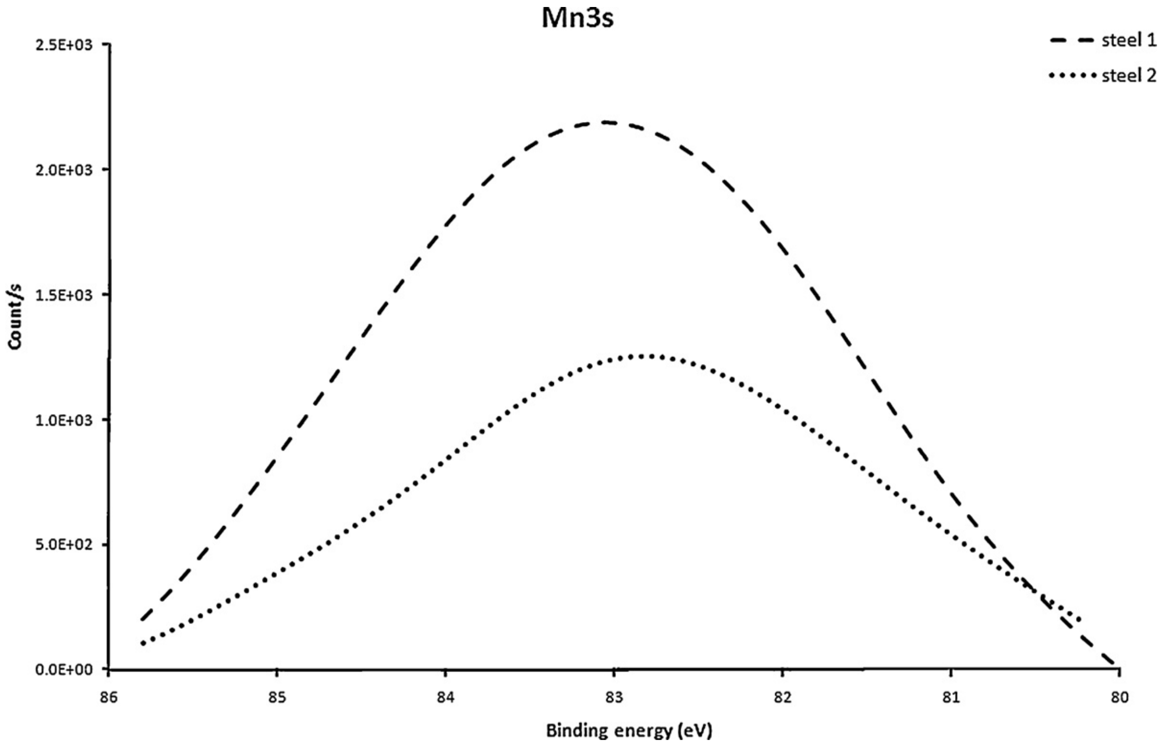

Fig. 7. XPS spectra of Mn3 s for the steels annealed at 0 °C dp.

annealed at −60, −30, and 0 °C dp. Eynde et al. [9] observed a high content of silicon on surface of steels annealed at 0 °C dp.

A Mo 4s peak relative to MoO_2 was identified on the surface of dual phase steel and of the experimental steel annealed at −30 °C dp, at 64.5 eV and 64.6 eV, respectively (Fig. 10). However, the GDOES analysis did not identify molybdenum on the surface of the modified steel (steel 2), and the content of Mo on the surface of the dual phase steel was the lowest at −30 °C dp. The XPS analysis showed that the Mo 4s peak of the dual phase steel had a higher intensity than the peak relative to steel 2. Both steels had the same

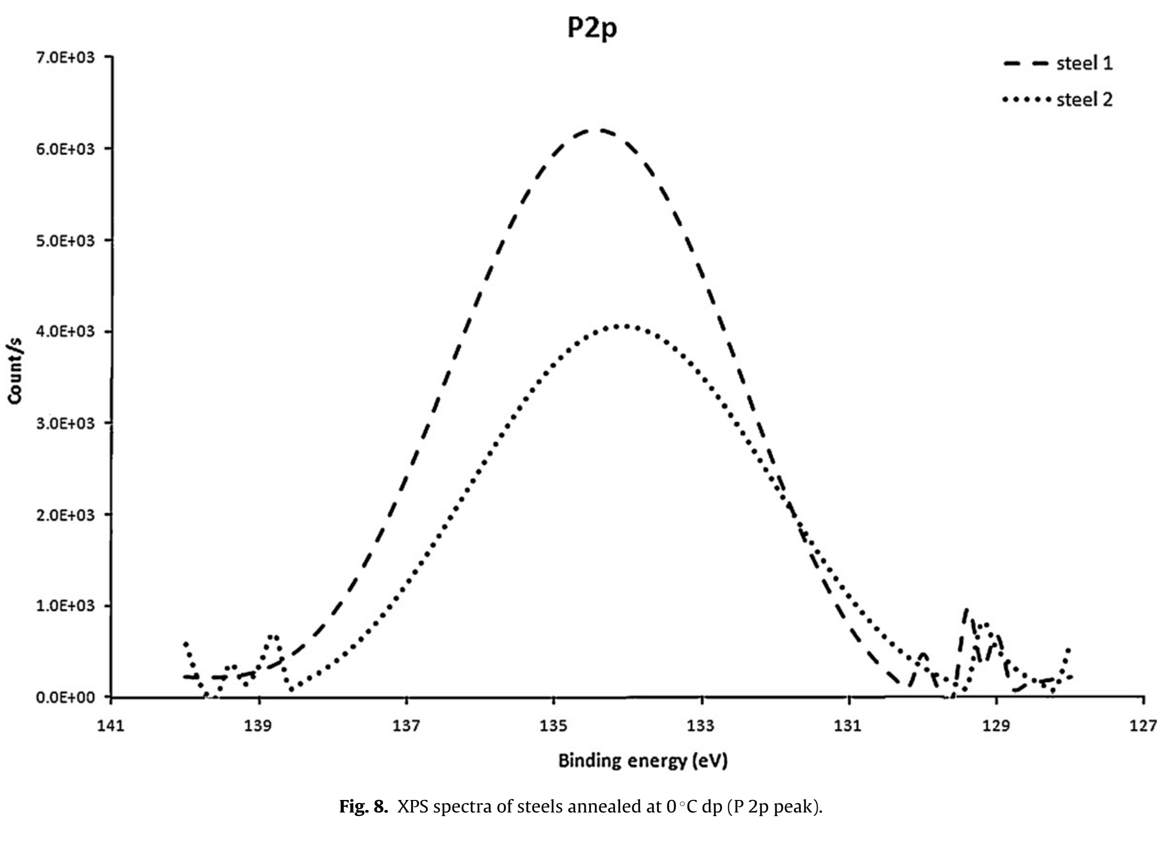

Fig. 8. XPS spectra of steels annealed at 0 °C dp (P 2p peak).

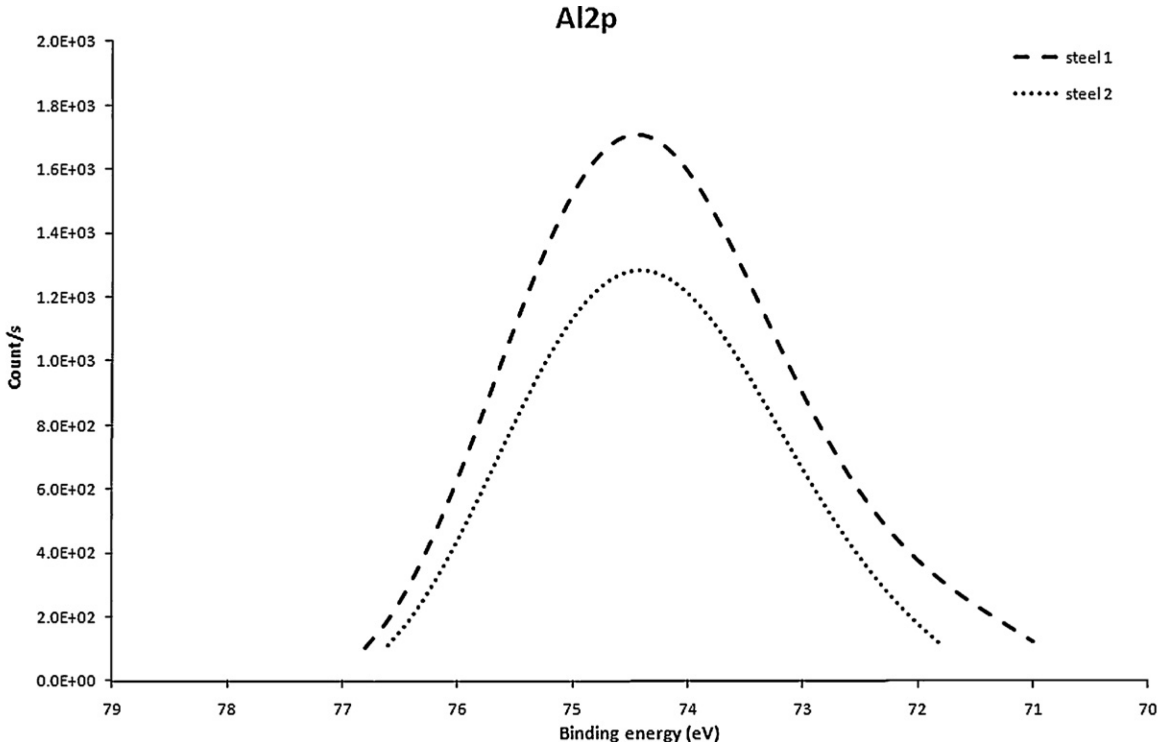

Fig. 9. XPS spectra of steels annealed at −60 °C dp (Al 2p peak).

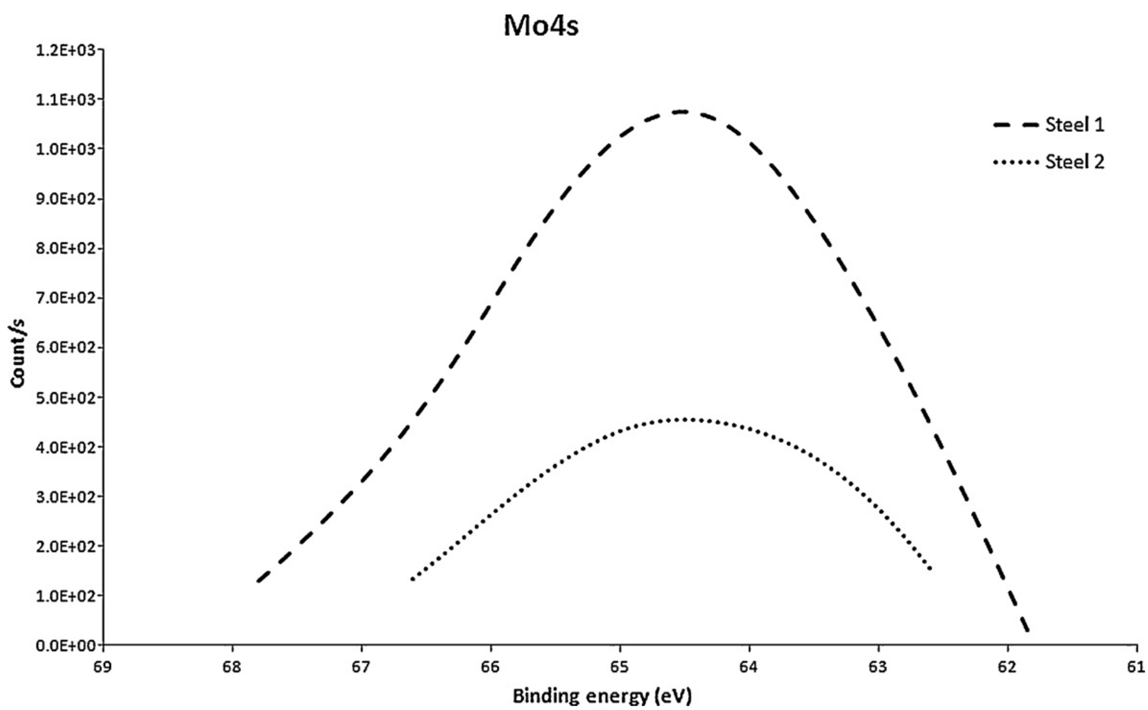

Fig. 10. XPS spectra of dual phase steel and of the experimental steel annealed at −30 °C dp, showing Mo 4s peak relative to MoO2, at 64,54 eV and 64,62 eV, respectively.

concentration of molybdenum (0.17% wt), indicating the effect of other parameters on segregation and oxidation of molybdenum.

4. Conclusions

The AFM analysis identified oxide agglomerates on the surfaces of both steels annealed at the dew points of −60, −30, and 0 °C.

External selective oxidation was observed for phosphorus on the steel surface annealed at 0 °C dp, and for manganese, silicon, and aluminum at a lower dew point.

The concentration of molybdenum of steels annealed at the dew points of −60, −30, and 0 °C increased as the depth from the surface of both steels increased.

The annealing of the experimental steel at 0 °C dp showed the lowest external oxidation on the steel surface.

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